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Crystal structure of 1-methyl-4-methylsulfanyl-1*H*-pyrazolo[3,4-*d*]pyrimidine

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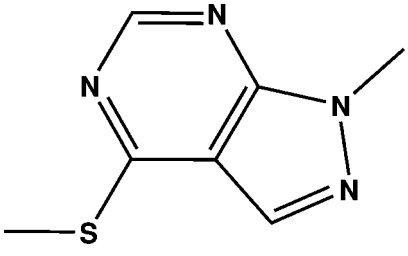
In the title compound, $C_7H_8N_4S$, the non-H atoms of the pyrazolo[3,4-*d*]pyrimidine ring system and the methylsulfanyl group lie on a crystallographic mirror plane. In the crystal, molecules are linked *via* a number of π–π interactions [centroid–centroid distances vary from 3.452 (7) to 3.6062 (8) Å], forming a three-dimensional structure.

Keywords: crystal structure; 1*H*-pyrazolo[3,4-*d*]pyrimidine; pharmacological and biochemical properties; π–π interactions.

CCDC reference: 1034638

1. Related literature

For similar compounds, see: El Fal *et al.* (2013, 2014*a*,*b*); Ouzidan *et al.* (2011). For pharmacological and biochemical properties of pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione derivatives, see: Chauhan & Kumar (2013); Venkatesan *et al.* (2014); Rashad *et al.* (2011).



2. Experimental

2.1. Crystal data

$C_7H_8N_4S$
M_r = 180.23
Orthorhombic, *Pbcm*
a = 7.9309 (14) Å
b = 15.335 (3) Å
c = 6.7158 (12) Å
V = 816.8 (3) Å^3
Z = 4
Mo *K*α radiation
μ = 0.34 mm^{-1}
T = 296 K
0.37 × 0.28 × 0.19 mm

2.2. Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.637, T_{max} = 0.746
2970 measured reflections
1227 independent reflections
1017 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.129
S = 1.09
1227 reflections
73 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5348).

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supporting information

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Crystal structure of 1-methyl-4-methylsulfanyl-1*H*-pyrazolo[3,4-*d*]pyrimidine

Mohammed El Fal, Youssef Ramli, El Mokhtar Essassi, Mohamed Saadi and Lahcen El Ammari

S1. Structural commentary

Synthesis of 1*H*-pyrazolo [3,4-*d*] pyrimidine-4-thiol derivatives has received considerable attention due to their biological activity especially as antimicrobial (Chauhan *et al.*, 2013), antitubercular (Venkatesan *et al.*, 2014) and anticancer (Rashad *et al.*, 2011) agents. During the search for new antibacterial agents synthesis, some 1*H*-pyrazolo[3,4-*d*] pyrimidine-4-thiol derivatives were prepared (El Fal *et al.*, 2013, 2014*a*, 2014*b*; Ouzidan *et al.*, 2011). These compounds are currently under investigation for possible biological activity.

The molecule of the title compound is build up from two fused five- and six-membered rings linked to methylsulfanyl group. All non hydrogen atoms of the molecule are coplanar as shown in Fig. 1. In the crystal, the molecules are linked together by a number of π–π interactions [centroid–centroid distances vary from 3.452 (7) to 3.6062 (8) Å], forming a three-dimensional structure.

S2. Synthesis and crystallization

To a solution of 1*H*-pyrazolo [3,4-*d*] pyrimidine-4-thiol (0.5 g, 3.28 mmol) dissolved in DMF (20 ml) was added iodomethane (0.43 ml, 6.62 mmol), potassium carbonate (0.93 g, 7.1 mmol) and a catalytic amount of tetra-n-butylammonium bromide (0.1 g, 0.4 mmol). The mixture was stirred for 48 h and monitored by thin layer chromatography. The mixture was filtered and the solvent was removed *in vacuo*. The solid obtained was crystallized from ethanol to give the title compound as orange crystals (yield: 65%).

S3. Refinement

The H atoms were located in a difference map and treated as riding with C—H = 0.93 Å (aromatic) and C—H = 0.96 Å (methyl), and with U_{iso}(H) = 1.2 U_{eq} (aromatic) and U_{iso}(H) = 1.5 U_{eq} (methyl).

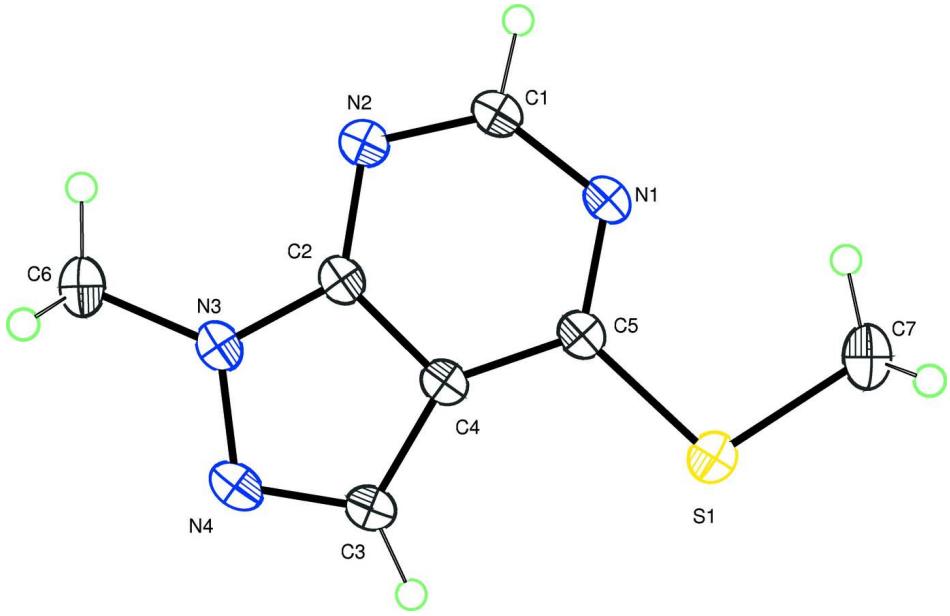

Figure 1

Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

1-Methyl-4-methylsulfanyl-1*H*-pyrazolo[3,4-*d*]pyrimidine

Crystal data

$C_7H_8N_4S$
M_r = 180.23
Orthorhombic, *Pbcm*
Hall symbol: -P 2c 2b
a = 7.9309 (14) Å
b = 15.335 (3) Å
c = 6.7158 (12) Å
V = 816.8 (3) Å^3
Z = 4
$F(000)$ = 376
D_x = 1.466 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1227 reflections
θ = 2.6–29.6°
μ = 0.34 mm^{-1}
T = 296 K
Block, orange
0.37 × 0.28 × 0.19 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.637, T_{max} = 0.746
2970 measured reflections
1227 independent reflections
1017 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 29.6°, θ_{min} = 2.6°
h = −10→4
k = −21→19
l = −3→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.129
S = 1.09
1227 reflections
73 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.3181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against all reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5519 (3)	0.06804 (13)	0.2500	0.0393 (5)
H1	0.4928	0.0156	0.2500	0.047*
C2	0.5516 (3)	0.21199 (12)	0.2500	0.0279 (4)
C3	0.7675 (3)	0.30515 (13)	0.2500	0.0322 (4)
H3	0.8763	0.3277	0.2500	0.039*
C4	0.7284 (2)	0.21512 (11)	0.2500	0.0264 (4)
C5	0.8115 (3)	0.13396 (11)	0.2500	0.0285 (4)
C6	0.3247 (3)	0.32714 (15)	0.2500	0.0450 (6)
H6A	0.3121	0.3658	0.1386	0.068*
H6B	0.2414	0.2818	0.2500	0.068*
C7	1.0858 (3)	0.02097 (16)	0.2500	0.0483 (6)
H7A	0.9865	−0.0148	0.2500	0.072*
H7B	1.1499	0.0095	0.1316	0.072*
N1	0.7221 (2)	0.06053 (10)	0.2500	0.0348 (4)
N2	0.4577 (2)	0.13910 (11)	0.2500	0.0369 (4)
N3	0.4970 (2)	0.29563 (11)	0.2500	0.0323 (4)
N4	0.6289 (3)	0.35277 (10)	0.2500	0.0349 (4)
S1	1.03110 (7)	0.13414 (4)	0.2500	0.0447 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0316 (10)	0.0218 (9)	0.0644 (15)	−0.0024 (7)	0.000	0.000
C2	0.0294 (9)	0.0221 (8)	0.0321 (9)	0.0016 (7)	0.000	0.000
C3	0.0301 (10)	0.0230 (8)	0.0434 (11)	−0.0032 (7)	0.000	0.000
C4	0.0280 (9)	0.0216 (8)	0.0295 (9)	−0.0008 (6)	0.000	0.000
C5	0.0295 (9)	0.0232 (9)	0.0329 (9)	0.0005 (7)	0.000	0.000
C6	0.0329 (11)	0.0330 (11)	0.0692 (16)	0.0095 (9)	0.000	0.000
C7	0.0376 (12)	0.0393 (12)	0.0680 (17)	0.0119 (10)	0.000	0.000
N1	0.0307 (9)	0.0199 (7)	0.0536 (11)	0.0005 (6)	0.000	0.000
N2	0.0290 (9)	0.0250 (9)	0.0568 (12)	−0.0015 (6)	0.000	0.000

N3	0.0318 (8)	0.0221 (7)	0.0429 (9)	0.0024 (6)	0.000	0.000
N4	0.0399 (10)	0.0211 (7)	0.0439 (10)	−0.0021 (6)	0.000	0.000
S1	0.0264 (3)	0.0316 (3)	0.0761 (5)	0.00110 (18)	0.000	0.000

Geometric parameters (Å, º)

C1—N2	1.321 (3)	C5—N1	1.331 (2)
C1—N1	1.355 (3)	C5—S1	1.741 (2)
C1—H1	0.9300	C6—N3	1.449 (3)
C2—N2	1.343 (3)	C6—H6A	0.9598
C2—N3	1.354 (2)	C6—H6B	0.9599
C2—C4	1.403 (3)	C7—S1	1.789 (3)
C3—N4	1.319 (3)	C7—H7A	0.9600
C3—C4	1.415 (2)	C7—H7B	0.9599
C3—H3	0.9300	N3—N4	1.365 (3)
C4—C5	1.408 (2)		
N2—C1—N1	129.3 (2)	C4—C5—S1	117.82 (14)
N2—C1—H1	115.3	N3—C6—H6A	107.7
N1—C1—H1	115.3	N3—C6—H6B	114.1
N2—C2—N3	127.68 (18)	H6A—C6—H6B	112.1
N2—C2—C4	125.63 (18)	S1—C7—H7A	110.8
N3—C2—C4	106.69 (17)	S1—C7—H7B	107.8
N4—C3—C4	110.97 (17)	H7A—C7—H7B	109.3
N4—C3—H3	124.5	C5—N1—C1	117.33 (17)
C4—C3—H3	124.5	C1—N2—C2	111.89 (18)
C2—C4—C5	115.96 (17)	C2—N3—N4	111.29 (17)
C2—C4—C3	104.60 (16)	C2—N3—C6	128.13 (19)
C5—C4—C3	139.45 (19)	N4—N3—C6	120.59 (17)
N1—C5—C4	119.88 (19)	C3—N4—N3	106.45 (16)
N1—C5—S1	122.30 (14)	C5—S1—C7	103.95 (11)